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(54) **Polyolefin-base resin composition for metal-product wrapping material.**

(57) Disclosed herein is a resin composition obtained by mixing an olefin-base resin, which has in turn been obtained by partially neutralizing a free carboxyl group in a random copolymer of an α -olefin and an α,β -ethylenically-unsaturated monocarboxylic or dicarboxylic acid, with a volatile rust preventive in a specific amount or more. The resin composition has excellent rust preventive properties and can hence be used advantageously as a wrapping material for metal products.

POLYOLEFIN-BASE RESIN COMPOSITION
FOR METAL-PRODUCT WRAPPING MATERIAL

Background of the Invention:

1) Field of the Invention:

5 This invention relates to a rust preventive resin composition suitable for use in formed or molded materials useful in covering, wrapping or packaging (hereinafter called "wrapping" collectively) various metal products which require rust prevention, such as
10 films, sheets, tubes and other packaging containers.

2) Description of the Prior Art:

Sheets and films with a rust preventive applied thereto have conventionally been known.

They include, for example, sheet-like materials,
15 such as paper and textile, with a rust preventive adhered or coated thereon or impregnated therein; films and sheets formed by subjecting a mixtures of a polyolefin-base resin and a rust preventive to melt extrusion molding; and the like.

20 The former rust preventive materials are however insufficient in rust preventive properties and the long acting property thereof in spite of the usual practice of incorporation of a rust preventive in relatively

high contents, because the paper and textile as base materials have high breathability and moisture permeability by themselves. It is hence necessary to laminate a material having low breathability and moisture permeability, such as a polyethylene film, or otherwise to use an additional outer wrapping material, thereby resulting not only in complicated wrapping work but also in a disadvantage in respect to wrapping costs.

On the other hand, the latter rust preventive materials encounter difficulties in dispersing the rust preventive in the resin uniformly at high contents due to the poor compatibility of the rust preventive with the polyolefin-base resin. This approach is therefore accompanied by such drawbacks that it cannot provide films having high rust preventive properties and in addition, the transparency, heat-sealing characteristics and the like of the resultant films per se are deteriorated.

With a view toward overcoming such drawbacks, it has also been proposed to combine a polar resin such as ethylene-ethyl acrylate copolymer, ethylene-acrylic acid copolymer or ethylene-vinyl acetate copolymer with a polyolefin-base resin so as to produce a rust preventive film improved in the compatibility and dispersibility of its associated rust preventive with

respect to the resin (Japanese Patent Publication No. 4295/1972). Although films obtained in accordance with this process are free of exudation or bleeding and exhibit long-acting rust preventive effects, they involve some practical problems as rust preventive wrapping films for metal products since the polar resin is highly corrosive to non-polar resins such as polyethylene and its corrosive properties becomes remarkable especially when maintained in contact with metals. The above-mentioned corrosive properties of the polar resin can be reduced to a certain extent by using the rust preventive in a large amount. Such excessive use of the rust preventive however leads to another problem that the transparency and heat-sealing characteristics of films are inevitably deteriorated.

It has also been proposed to produce a rust preventive film by adding and mixing an organic amine and an acid with a polyolefin resin and then heating and melt-molding the resultant composition so that a volatile rust preventive consisting of the acid salt of the organic amine is formed by the reaction of the organic amine and acid in the course of the molding step, thereby allowing the rust preventive to be dispersed uniformly in the resin (Japanese Patent Publication No. 2449/1978). This process is very effective in dispersing the volatile rust preventive

uniformly in the resin. It is however accompanied by such problems that the rust preventive undergoes bleeding to the surfaces of the film along the passage of time and hence deteriorates the transparency and heat-sealing characteristics of the film per se.

Summary of the Invention:

With a view toward solving the above-mentioned problems observed in rust preventive resin compositions useful as wrapping materials for metal products, an object of this invention is to provide a rust preventive resin composition which features extremely good compatibility between the resin itself and a volatile rust preventive and hence permits uniform dispersion of the rust preventive at a high content and when formed into a film, has excellent properties as a wrapping material such as excellent rust preventive effects and good heat-sealing characteristics.

The present inventors have carried out an investigation on such resin compositions and have succeeded in obtaining a rust preventive resin composition having the above-described properties and characteristics by selecting and using a polyolefin-base resin, which has been obtained by neutralizing to a specific degree a free carboxyl group in a random copolymer of an α -olefin and an

- 5 -

α,β -ethylenically-unsaturated monocarboxylic or dicarboxylic acid with ions of an alkali metal or alkaline earth metal having a normal electrode potential lower than aluminum, and adding and mixing a
5 volatile rust preventive with the polyolefin-base resin, leading to completion of this invention.

The present invention will hereinafter be described in detail.

Detailed Description of the Invention:

10 The present invention provides a rust preventive resin composition suitable for use in a wrapping material, comprising:

an olefin-base resin obtained by partially neutralizing a free carboxyl group in a random
15 copolymer of an α -olefin and an α,β -ethylenically-unsaturated monocarboxylic or dicarboxylic acid, the latter being contained in an amount of 1.0 - 20 mole %, with ions of an alkali metal or alkaline earth metal having a normal electrode potential lower than aluminum
20 to a level in a range of 5 - 90 mole % based on the original content of the free carboxyl group; and

a volatile rust preventive in an amount of at least 0.5 parts by weight per 100 parts by weight of the olefin-base resin.

of an ethylene-acrylic acid copolymer, 5 parts of cyclohexylammonium benzoate were added and mixed. The resultant resin composition was formed at an extrusion temperature of 140 - 160°C into a tubular film having a thickness of 0.1 mm by an inflation extruder. The thus-obtained film had good transparency and upon its extraction with warm water, the formation of sodium benzoate was confirmed.

Examples 2 - 3:

10 To 100 parts of a base resin consisting of powder of a sodium salt resin (M.I. = 2.8; density = 0.95; "HI-MILAN 1605", trade name; commercial product of Du Pont-Mitsui Polychemicals Co., Ltd.) of an ethylene-methacrylic acid copolymer or powder of a
15 magnesium salt resin (M.I. = 0.9; density = 0.940; "COPOLENE D-200", trade name; commercial product of Asahi-Dow, Limited) of an ethylene-acrylic acid copolymer, 10 parts of dicyclohexylammonium nitrite were added and mixed. By a T-die extruder, the
20 resultant resin composition was formed at an extrusion temperature of 140 - 160°C into a film having a thickness of 0.1 mm.

The thus-obtained films were good in transparency and upon their extraction with warm water, the formation of sodium nitrite and that of magnesium nitrite were confirmed.

Example 4:

To 100 parts of a base resin consisting of powder of the sodium salt resin (M.I. = 2.8; density = 0.95; "HI-MILAN 1605", trade name; commercial product of Du Pont-Mitsui Polychemicals Co., Ltd.) of the ethylene-methacrylic acid copolymer, 5 parts of dicyclohexylammonium phosphate were added and mixed. By an inflation extruder, the resultant mixture was formed at an extrusion temperature of 140 - 160°C into a film having a thickness of 0.1 mm. The film was good in transparency and upon its extraction with warm water, the formation of sodium phosphate was confirmed. Comparative Examples 1 - 3:

To 100 parts of a low-density polyethylene (M.I. = 1.0, density = 0.920; "YUKALON YF-30", trade name; commercial product of Mitsubishi Petrochemical Co., Ltd.), an ethylene-ethyl acrylate copolymer resin (M.I. = 1.5; density = 0.93; "DPDJ-6182", trade name; commercial product of Nippon Unicar Co., Ltd.) or a zinc salt resin (M.I. = 1.5; density = 0.94; "HI-MILAN 1650", trade name; commercial product of Du Pont-Mitsui Polychemicals Co., Ltd.) of an ethylene-methacrylic acid copolymer as a base resin, 5 parts of cyclohexylammonium benzoate were added and mixed in the same manner as in Example 1. Following the procedure of Example 1, a film having a thickness of 0.1 mm was

- 14 -

formed. In the film obtained by using the low-density polyethylene as a base resin (Comparative Example 1), the state of dispersion of the added rust preventive was extremely poor and the film was hence whitened. In

5 each of the films obtained respectively by using the ethylene-ethyl acrylate copolymer resin (Comparative Example 2) and the zinc salt resin of the ethylene-methacrylic acid copolymer (Comparative Example 3) as base resins, the state of dispersion of the rust
10 preventive was relatively good.

Comparative Example 4:

To 100 parts of the same base resin as that employed in Comparative Example 2, were added 5 parts of cyclohexylammonium benzoate as a vapor-phase rust
15 preventive and 1 part of sodium benzoate as an in-contact rust preventive. The resultant mixture was formed into a film having a thickness of 0.1 mm in the same manner as in Example 1. In the thus-obtained film, the dispersion of the sodium benzoate was poor
20 and a number of white spots occurred in the film.

Comparative Example 5:

To 100 parts of the same ethylene-ethyl acrylate copolymer resin as that employed in Comparative Example 2, 10 parts of dicyclohexylammonium
25 nitrite were added and mixed. Following the same procedure as in Examples 2 - 3, a film having a

- 15 -

thickness of 0.1 mm was formed. The rust preventive
bled partly in the thus-obtained film, and the film
lost transparency significantly.

The compositions and performance of the films
5 obtained in Examples 1 - 4 and Comparative
Examples 1 - 5 are summarized in Tables 1 and 2 respectively.

The rust preventive effects of each film shown
in Table 2 were evaluated by the following testing
method.

10 Testing method:

By using two cold-rolled steel sheets (60 mm x 80
mm x 1 mm) prescribed in JIS G-3141, they were fastened
to each other in their four corners by iron screws in
such a way that they were parallel to each other with
15 an interval of 25 mm, thereby fabricating a structure
as a sample to be wrapped. After washing samples of
the same structure with warm naphtha and warm methanol
in order, they were wrapped by the
individual films and hermetically sealed by heat-
20 sealing the films. The thus-wrapped samples were
suspended in a humidity cabinet maintained at $50 \pm$
 1°C and 100% RH to conduct an accelerated test for 120
days. In order to evaluate the in-contact rust
preventive properties and vapor-phase rust preventive
25 properties at the same time, the above-mentioned
structure was used as the sample to be wrapped.

Namely, the mutually-facing surfaces (inner surfaces) of both sheets permitted evaluation of the vapor-phase rust preventive properties because they did not contact the film directly. The opposite surfaces (outer surfaces) were brought into direct contact with the film, thereby enabling evaluation of the in-contact rust preventive properties.

Table 1 Film Composition

	Base resin	Volatile rust preventive (content)
Example 1	Ethylene-acrylic acid sodium salt copolymer	Cyclohexylammonium benzoate (5)
Example 2	Ethylene-methacrylic acid sodium salt copolymer	Dicyclohexylammonium nitrite (10)
Example 3	Ethylene-acrylic acid magnesium salt copolymer	ditto (10)
Example 4	Ethylene-methacrylic acid sodium salt copolymer	Dicyclohexylammonium phosphate (5)
Comp. Ex. 1	Low-density polyethylene	Cyclohexylammonium benzoate (5)
Comp. Ex. 2	Ethylene-ethyl acrylate copolymer	ditto (5)
Comp. Ex. 3	Ethylene-methacrylic acid zinc salt copolymer	ditto (5)
Comp. Ex. 4	Ethylene-ethyl acrylate copolymer	Cyclohexylammonium benzoate (5) Sodium benzoate (1)
Comp. Ex. 5	ditto	Dicyclohexylammonium nitrite (10)

1) The content of each rust preventive is expressed in terms of parts by weight per 100 parts by weight of its corresponding base resin.

2) Each film thickness was 0.1 mm.

Table 2

	Rust preventive effects 1)		Haze 2) (%)	Strength of heat- seal, g/15 mm width 3)
	Surface in contact with film (contact)	Surface out of contact with film (vapor phase)		
Ex. 1	No rusting over 120 days	No rusting over 120 days	13	1,700
Ex. 2	ditto	ditto	18	1,950
Ex. 3	ditto	ditto	8	2,040
Ex. 4	ditto	ditto	15	1,500
Comp. Ex. 1	Rusted on 35th day	Rusted on 55th day	55	390
Comp. Ex. 2	Rusted on 16th day	Rusted on 48th day	25	520
Comp. Ex. 3	Rusted on 1st day	Rusted on 75th day	18	1,600
Comp. Ex. 4	Rusted on 18th day	Rusted on 45th day	49	430
Comp. Ex. 5	Rusted on 25th day	Rusted on 60th day	37	330

- 1) The percentage of rust occurred per unit area was determined by JIS Z-2912. The rust preventive effects are shown in terms of the number of days to reach 10%.
- 2) Measurement was conducted following the method prescribed in ASTM D-1003.
- 3) Measurement was conducted by a heat sealability testing machine manufactured by Toyo Tester Co., Ltd. Sealing conditions: temperature = 140°C, pressure = 2.0 kg/cm², time = 1.0 second.

The resin compositions of this invention had numerous practical merits as rust preventive wrapping materials such that they showed extremely good rust preventive effects compared with those employed in the Comparative Examples and composed in combination with the other polar resins and their formed products, namely, films were by themselves good in transparency and heat-sealing characteristics as readily envisaged from Table 2; and moreover, they featured easy processing upon production of the films without developing the problem of environmental contamination due to smoking, scattering and the like of the volatile rust preventives by their evaporation.

CLAIMS:

1. A rust preventive resin composition suitable for use in a wrapping material, comprising:

an olefin-base resin obtained by partially
5 neutralizing a free carboxyl group in a random
copolymer of an α -olefin and an α,β -ethylenically-
unsaturated monocarboxylic or dicarboxylic acid, the
latter being contained in an amount of 1.0 - 20 mole %, with ions of an alkali metal or alkaline earth metal
10 having a normal electrode potential lower than aluminum to a level in a range of 5 - 90 mole % based on the original content of the free carboxyl group; and
a volatile rust preventive in an amount of at least 0.5 parts by weight per 100 parts by weight of
15 the olefin-base resin.

2. A rust preventive resin composition according to Claim 1, wherein the ions are sodium ions or magnesium ions.

3. A rust preventive resin composition according to Claim 1, wherein the volatile rust preventive is
20 selected from the group consisting of amine salts of organic carboxylic acids, nitrous acid, phosphoric acid and carbonic acid.